

MANUFACTURE OF ELECTRONIC COMPONENT WITH ELECTROLESS PLATED FILM

Publication number: JP8264372

Publication date: 1996-10-11

Inventor: KANAI HIDEYUKI; ITO MITSUYOSHI; HONDA TOSHIMITSU

Applicant: TAIYO YUDEN KK

Classification:

- international: C23C18/16; C23C18/52; H01C7/02; H01C7/04; H01C17/28; H01F27/29; H01F41/02; H01G4/12; H01F41/02; C23C18/16; H01C7/02; H01C7/04; H01C17/28; H01F27/29; H01F41/02; H01G4/12; H01F41/02; (IPC1-7): H01F41/02; H01G4/12; C23C18/16; C23C18/52; H01C7/02; H01C7/04; H01C17/28; H01F27/29

- European:

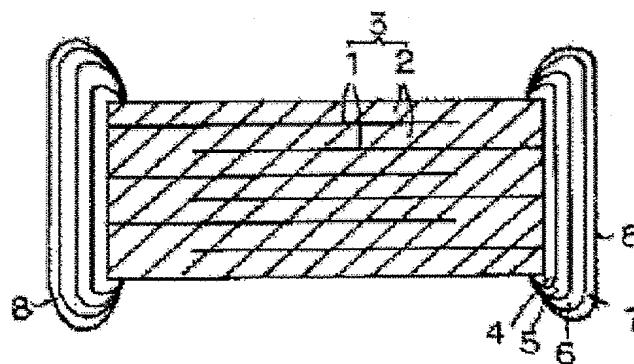
Application number: JP19950084626 19950317

Priority number(s): JP19950084626 19950317

Report a data error here

Abstract of JP8264372

PURPOSE: To reduce the variation in thickness and also lower film hardness by forming an electroless plated film using an electroless plating liquid having more oxygen than a normal oxygen concentration or having the electroless plated film obtained using an electroless plating liquid having normal oxygen concentration subjected to additional thermal treatment. **CONSTITUTION:** A baked conductive film 4 is formed by applying nickel conductive paste to both ends of a ceramic material 3 comprising internal electrodes 1 and ceramic inductors 2 alternately laminated and baking them. Then the material 3 is soaked in an electroless copper plating liquid and stirred in the air to form an electroless copper plated film 5 on the conductive film 4. Then after the material is rinsed in water, electrolytic nickel barrel plating is applied in nickel plating bath to form a nickel plated film 6. This material is further subjected to electrolytic solder barrel plating in solder plating bath to form a solder plated film 7, thereby forming external electrodes 8, 8.



Data supplied from the esp@cenet database - Worldwide

(19)日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11)特許出願公開番号

特開平8-264372

(43)公開日 平成8年(1996)10月11日

(51)Int.Cl. ⁶	識別記号	庁内整理番号	F I	技術表示箇所
H 0 1 G 4/12	3 6 4		H 0 1 G 4/12	3 6 4
C 2 3 C 18/16			C 2 3 C 18/16	C
18/52			18/52	Z
H 0 1 C 7/02			H 0 1 C 7/02	
7/04			7/04	
審査請求 未請求 請求項の数 5 F D (全 10 頁) 最終頁に続く				

(21)出願番号 特願平7-84626

(22)出願日 平成7年(1995)3月17日

(71)出願人 000204284

太陽誘電株式会社

東京都台東区上野6丁目16番20号

(72)発明者 金井 秀幸

東京都台東区上野6丁目16番20号 太陽誘電株式会社内

(72)発明者 伊藤 光由

東京都台東区上野6丁目16番20号 太陽誘電株式会社内

(72)発明者 本多 敏光

東京都台東区上野6丁目16番20号 太陽誘電株式会社内

(74)代理人 弁理士 佐野 忠

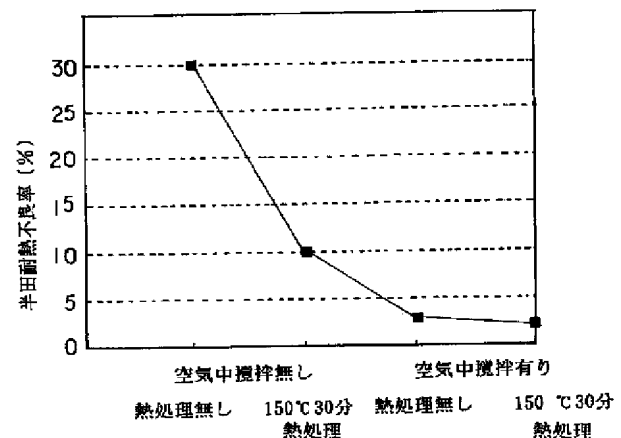
(54)【発明の名称】 無電解メッキ膜付電子部品の製造方法

(57)【要約】

【目的】例えばチップ状電子部品の外部電極のメッキ膜の膜厚を均一にすることができるようにし、しかもヒートサイクル試験や熱衝撃試験による熱応力に耐えられるようにするために無電解メッキ膜を利用すること。

【構成】通常より酸素濃度の高い無電解メッキ液を用いてメッキ膜を形成するか、通常の酸素濃度の無電解メッキ液を用いてメッキ膜を形成しさらに熱処理する。また、両方を行う。

【効果】無電解メッキ膜の延性が増加し、膜硬度が低下する。これによりヒートサイクル試験や熱衝撃試験による熱応力に耐えられる無電解メッキ膜が得られる。



【特許請求の範囲】

【請求項1】 無電解メッキ膜を空気存在下の無電解メッキ液に通常含有される溶存酸素の量より多い酸素を有する無電解メッキ液を用いて形成する高酸素無電解メッキ工程及び空気存在下の無電解メッキ液に通常含有される溶存酸素以下の酸素を含有する無電解メッキ液を用いて形成した後熱処理を行う熱処理併用無電解メッキ工程の少なくとも1つの工程を含む無電解メッキ膜形成工程を有する無電解メッキ膜付電子部品の製造方法。

【請求項2】 無電解メッキ膜を空気存在下の無電解メッキ液に通常含有される溶存酸素の量より多い酸素を有する無電解メッキ液を用いて形成する高酸素無電解メッキ工程と、熱処理工程を含む無電解メッキ膜形成工程を有する無電解メッキ膜付電子部品の製造方法。

【請求項3】 熱処理工程は150～250℃、30分から120分である請求項1又は2記載の無電解メッキ膜付電子部品の製造方法。

【請求項4】 少なくともセラミック素体に外部電極を有する電子部品の製造方法において、該外部電極は錫含有メッキ層を表面層に有する複数の導電層からなり、かつ該複数の導電層の少なくとも1層は請求項1ないし3のいずれかに記載の無電解メッキ膜形成工程により形成される無電解メッキ膜付電子部品の製造方法。

【請求項5】 複数の導電層は下地層と錫含有メッキ層の表面層の少なくとも2層を有し、該下地層は塗布膜による厚膜からなる請求項1ないし4のいずれかに記載の無電解メッキ膜付電子部品の製造方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、チップ状積層コンデンサ等の電子部品において、外部電極に無電解メッキ膜を有する電子部品の製造方法に関するものである。

【0002】

【従来の技術】コンデンサやインダクタ等の電子部品は多くの電子機器に用いられているが、最近の電子機器の小型化に伴って、プリント基板に電子部品を高密度に実装した回路部品が用いられるようになり、この高密度に実装するための電子部品として例えばチップ状の積層セラミックコンデンサ、チップ状のセラミックサーミスタ、チップ状のインダクタ等のチップ状電子部品が多く用いられている。これらのチップ状電子部品は、それぞれの素子の角柱タイプや円柱タイプのセラミック素体の両端面に外部電極を形成したものであり、これら外部電極がプリント基板のはんだ付けランドにはんだ付けされて使用される。例えばチップ状の積層セラミックコンデンサは、セラミック誘電体層と内部電極が交互に積層され、その積層体のセラミック素体の両側端面に当該内部電極の端部が一つおきに互いに反対側になるように引き出され、その端部に接続する外部電極が当該端面に形成

され、この外部電極がプリント基板のはんだ付けランドにはんだ付けされて使用される。このチップ状積層セラミックコンデンサやその他のチップ状電子部品の外部電極を形成するには、Ag、Ag-Pd、Cu、Ni等を含有する焼付け型導電ペーストをそれぞれのセラミック素体の両側端面に塗布して焼付け、厚膜の下地層を形成する。次に、この焼付け膜だけでは、プリント基板のはんだ付けランドにはんだ付けされるときに、溶融はんだにAgが溶解して移行し、その焼付け膜を痩せさせる、いわゆる「はんだ食われ」の現象を生じるので、この焼付け膜の上にNi、Cuなどの金属のメッキを施すことが行われており、さらにそのメッキ層では溶融はんだを良く濡らすことができず、実用性のあるはんだ付け強度が得られないので、そのメッキ層の上に溶融はんだに対する濡れ性を高めるためのSnあるいはSnとPbからなるはんだをメッキすることが一般的に行われている。

【0003】

【発明が解決しようとする課題】これらのチップ状電子部品のメッキ層は、電解メッキにより形成されているが、そのメッキ層を下地層を介して設けるのはセラミック等の不導体には直接電解メッキを行うことができないからであり、その下地層は上記したように塗布膜からなる厚膜であるので、例えばニッケルの焼付け型導電ペーストを用いた厚膜ではその表面に凹凸を生じることを避けることができない。その凹凸のある表面に電解メッキを施すと、凸部分におけるメッキ電流密度が大きくなってメッキ膜が厚く形成され、凹部分におけるメッキ電流密度が小さくなってメッキ膜が薄く形成されるので、メッキ電流密度がばらつき、それにしがつてメッキ膜の膜厚もばらつき、いわゆるメッキの付きまわり性が悪く、均質なメッキ膜が得られ難く、その結果チップ状電子部品をプリント基板にはんだ付けするときにはんだの濡れ性を悪くすることがある。また、例えば積層LCチップ部品では、図9に示すL₁、L₂のインダクタとCのコンデンサをT型に接続したT型LC回路の場合、図10に示すように、インダクタ部11、コンデンサ部12を積層し、前者を左右一対のコイル13、14を接続して構成し、後者を誘電体を上下一対の内部電極15、16により挟持して構成し、その積層体の外壁に上記LC回路のLC接続部分の②に対応する外部電極17、同様にL₁、L₂の端子①、③に対応するコイル13、14のそれぞれの端子に外部電極18、19、同様にCの端子④に対応するコンデンサの内部電極の端子に外部電極20をそれぞれ設けた構造のものが製造されているが、その外部電極は焼付け型導電ペースト膜の上にいわゆるバレル電解メッキを行ったものであり、バレル電解メッキは、メッシュのバレルの中に陰極を設け、これに対応してバレルの外部に設けた陽極との間にメッキ浴を介在させ、バレルにメッキ対象物と粒状の導体のダミーを入れ、これらを一緒に攪拌しながらメッキを行うもの

である。そのため、図9からも知られるように、 L_1 、 L_2 の端子①、③及びその接続部②はこれらのいずれか一つが陰極と電氣的に導通されると他の端子も電氣的に導通されるが、コンデンサCの端子④はこれらとは電氣的に絶縁されており、④の部分が導通される確率は①～③の場合の1/3になり、その結果①～③に対応する上記外部電極17～19はメッキ膜が厚くなり、④に対応する外部電極20のメッキ膜は薄くなり、メッキ膜の厚さにばらつきを生じ、上記と同様な問題を生じる。

【0004】このような電解メッキ方法によらないメッキ方法として、例えば電子部品としてプリント配線板を製造する場合には、ガラス、陶磁器、プラスチックなどの不導体表面に導電性を与える金属層を形成する場合と同様に、無電解メッキ方法が銀鏡反応と同様に用いられているが、特に半導体素子の高集積化と、表面実装化に伴い、高密度配線、高多層化が求められているプリント配線板の微細回路形成や高アスペクト比の小径の穴に対するスルホールメッキを無電解銅メッキにより施すことが行われている。プリント配線板に形成される無電解銅メッキ膜としては、寒暖が繰り返し行われたり、急激に温度変化させた場合でもそのメッキ膜にクラックが入ったり、そのメッキ膜が基板から剥離しないような物性、すなわちヒートサイクル試験や熱衝撃試験における熱応力に耐える性質が求められており、そのためには延性が高いことが必要であると言われている。しかしながら、従来の空気存在下のメッキ浴で無電解メッキを行う無電解メッキ法では、その高い延性のメッキ膜が得られず、上記の試験による熱応力によりメッキ膜にクラックが生じたり、メッキ膜が基板から剥離するということが起こり、不良品を作ることがあった。

【0005】本発明の第1の目的は、膜厚のばらつきの少ない無電解メッキ膜を有する無電解メッキ膜付電子部品を提供することにある。本発明の第2の目的は、はんだの濡れ性が優れた無電解メッキ膜を有する無電解メッキ膜付電子部品を提供することにある。本発明の第3の目的は、延性が高く、硬度が低い無電解メッキ膜を有する無電解メッキ膜付電子部品を提供することにある。本発明の第4の目的は、ヒートサイクル試験や熱衝撃試験における熱応力に耐えることができる無電解メッキ膜を有する無電解メッキ膜付電子部品を提供することにある。

【0006】

【課題を解決するための手段】本発明は、上記課題を解決するために、(1)、無電解メッキ膜を空気存在下の無電解メッキ液に通常含有される溶存酸素の量より多い酸素を有する無電解メッキ液を用いて形成する高酸素無電解メッキ工程及び空気存在下の無電解メッキ液に通常含有される溶存酸素以下の酸素を含有する無電解メッキ液を用いて形成した後熱処理を行う熱処理併用無電解メッキ工程の少なくとも1つの工程を含む無

電解メッキ膜形成工程を有する無電解メッキ膜付電子部品の製造方法を提供するものである。また、本発明は、

(2)、無電解メッキ膜を空気存在下の無電解メッキ液に通常含有される溶存酸素の量より多い酸素を有する無電解メッキ液を用いて形成する高酸素無電解メッキ工程と、熱処理工程を含む無電解メッキ膜形成工程を有する無電解メッキ膜付電子部品の製造方法、(3)、熱処理工程は150～250℃、30分から120分である上記(1)又は(2)の無電解メッキ膜付電子部品の製造方法、(4)、少なくともセラミック素体に外部電極を有する電子部品の製造方法において、該外部電極は錫含有メッキ層を表面層に有する複数の導電層からなり、かつ該複数の導電層の少なくとも1層は上記(1)ないし(3)のいずれかの無電解メッキ膜形成工程により形成される無電解メッキ膜付電子部品の製造方法、

(5)、複数の導電層は下地層と錫含有メッキ層の表面層の少なくとも2層を有し、該下地層は塗布膜による厚膜からなる上記(1)ないし(4)のいずれかの無電解メッキ膜付電子部品の製造方法を提供するものである。

【0007】本発明において、「無電解メッキ膜」とは、「無電解メッキ液」によるメッキ処理により得られるメッキ膜であるが、「無電解メッキ液」とはメッキ用金属イオン、還元剤、錯化剤及びアルカリ剤を少なくとも含有する無電解メッキ液をいう。ここで、メッキ用金属イオンとは、被処理物にメッキしようとする金属のイオンであり、例えば銅メッキをする場合は銅イオンであるが、これに限らず金(Au)の無電解メッキ、白金(Pt)の無電解メッキ、銀(Ag)の無電解メッキ、パラジウムの無電解メッキ、これらの合金その他の金属の無電解メッキ等の無電解金属メッキを行うことができ、これらの場合にはAuイオン、Ptイオン等の金属イオンをいう。これらの金属イオンの対イオンは、硫酸イオン、硝酸イオン、塩素イオン等の鉍酸イオン、シアニオン、ピロリン酸イオン等が挙げられるが、その供給を行うには、例えばCuイオンの場合は硫酸銅、硝酸銅、塩化銅塩、シアニ化銅、ピロリン酸銅塩等の溶液があり、特に第2銅塩が好ましいが、金属銅、銅の酸化物等他の銅化合物を硫酸等の鉍酸溶液に溶解させて供給するようにしても良く、他の金属イオンの場合もこれに準じて行うことができる。無電解メッキ液中の金属イオンの濃度としては、5g/リットル～10g/リットルが好ましい。これより多いと、メッキ液中で金属の析出反応が生じ易く、これより少ないと被処理物に対するメッキの金属の析出反応が低くなり易い。

【0008】また、還元剤は、無電解メッキ液中のメッキしようとする金属イオンを還元してその金属を被処理物表面に析出させ、金属膜を形成できる化合物をいうが、具体的にはホルマリン、パラホルムアルデヒド、ジメチルアミンボラン、次亜リン酸塩、ヒドラジン、グリ

オキシル酸、 KBH_4 、 NaBH_4 、ロッシュエル塩等が挙げられる。これらは単独又は複数併用できる。無電解メッキ液中の還元剤の濃度としては、 $0.1\text{ g/リットル} \sim 20\text{ g/リットル}$ が好ましい。これより多いと、メッキ液中で金属の析出反応が生じ易く、これより少ないと被処理物に対するメッキの金属の析出反応が低くなり易い。アルカリ剤としては、 NaOH 、 KOH 、 LiOH 等のアルカリ金属の水酸化物が好ましく、メッキ液の pH が $11.0 \sim 13.0$ になるように添加することが好ましい。錯化剤は、錯体を形成することができる物質をいうが、具体的には、例えば酒石酸塩、 EDTA （エチレンジアミン四酢酸）、 NTA （ニトリロ酢酸）、 HEDTA （オキシエチルエチレンジアミン三酢酸）、 DHEDDA （ジヒドロキシエチルエチレンジアミン二酢酸）、 $1,3\text{PDTA}$ （ $1,3$ -プロベンジアミン四酢酸）、 DTPA （ジエチレントリアミン五酢酸）、 TTHA （トリエチレンテトラミン六酢酸）、 HIMDA （ヒドロキシエチルイミノ二酢酸）、アンモニア等の化合物であって、金属、特に Cu 等の遷移金属と錯体を形成することができる化合物が挙げられる。無電解メッキ液には安定剤を使用することも好ましく、この安定剤としては、 DDCN （ジエチルジチオカルバミン酸ナトリウム）、 KSCN （チオシアン化カリウム）、 $2,2'$ -ビピリジル、 $2,2'$ -ジピリジン、ニコチン酸、チオ尿素、テトラメチルチオ尿素、クブロン、クペロン、チアゾール、 2 -メルカプトベンゾチアゾール、フェロシアン化カリウム、フェリシアン化カリウム、シアン化ナトリウム、ピロール、ピラゾール、イミダゾール、 $1,2,4$ -トリアゾール、 $1,2,4$ -ベンゾトリアゾール、チオフエン、チオメリッド、ロダニン、ルベアン酸、ピリジン、トリアジン、メチルオレンジ、ベンゾキノリン、 $2,2'$ -ビキノリン、ジチゾン、ジフェニルカルバジド、ネロクプロイン、 $2(2$ -ビピリジル)イミダゾリン、 $1,10$ -フェナンスロリン等のシアン化合物、窒素系有機化合物、イオウ化合物等を添加することが好ましく、これらは単独又は複数併用される。無電解メッキ液中の安定化剤の濃度としては $0.01 \sim 100\text{ ppm}$ が好ましい。これより多いと被処理物に対するメッキ反応が停止し易く、これより少ないとそのメッキ反応が起こり難くなる。

【0009】本発明において、「空気存在下の無電解メッキ液に通常含有される溶存酸素の量」とは、無電解メッキ液を用いてメッキ処理を行う場合にそのメッキ液に含有される酸素の量であり、その濃度は 1 ppm 以下が挙げられる。また、その溶存酸素の量「より多い酸素を有する無電解メッキ液」とは、具体的には空気や酸素を無電解メッキ液中にバブリングしたり、オゾンを吹き込んだり、過酸化水素を含有させる等によりその酸素を 1 ppm より多い状態にすることをいい、例えば $4 \sim 6\text{ ppm}$ が挙げられるが、溶存酸素である場合のみな

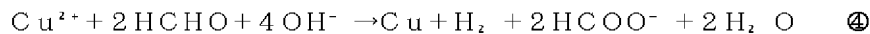
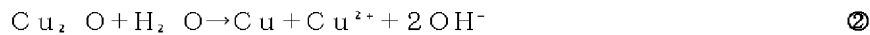
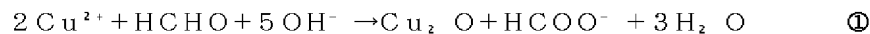
らず、その無電解メッキ液中に存在できるものでも良く、その際加圧して溶解量を高めるようにしても良い。この酸素の量が少な過ぎると、無電解メッキ膜の延性は高くなり、硬度は低くなり、多すぎるとメッキ膜そのものを酸化するので好ましくない。

【0010】本発明において、電子部品としては高密度配線、高多層化用の微細回路形成や高アスペクト比の小径の穴のスルホール用無電解メッキ膜を有するプリント配線基板等の配線基板や、少なくともセラミック素体に外部電極を有する電子部品が挙げられるが、後者としては特にチップ状セラミック電子部品が挙げられ、これらには、チップ状円筒形コンデンサ、チップ状抵抗体、チップ状フェライトビーズインダクタ、 NTC 又は PTC 型のチップ状サーミスタ、チップ状バリスター、チップ状積層電子部品等が挙げられ、チップ状積層電子部品としては、チップ状積層セラミックコンデンサ、チップ状積層セラミックインダクタ、チップ状積層セラミクトランス、チップ状積層セラミック LC 部品等が挙げられる。なお、「電子部品」を「コンデンサとインダクタを内蔵し、それぞれの外部電極間が電氣的に導通する回路と直流では電氣的に遮断する回路を有する電子部品」とすることもできる。本発明において、セラミック素体とは、セラミック材料の焼成体を主体としたものをいうが、これを用いた電子部品がサーミスタの場合は抵抗体、フェライトビーズの場合は導体の磁性体による被覆体、積層セラミックコンデンサの場合はセラミック層を内部電極を挟んで積層した積層体、積層セラミックインダクタ、積層セラミクトランスの場合はセラミック層を内部導体を挟んで積層した積層体をいい、その他の電子部品のセラミック素体もこれらに準ずる。

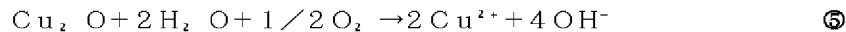
【0011】本発明において、「少なくともセラミック素体に外部電極を有する」とは、例えば上記セラミック素体の両端部に外部電極を有する場合のみならず、外部電極間のセラミック素体に絶縁膜を有するような場合もいう。外部電極はセラミック素体に形成される導電層の下地層と、錫含有メッキ層の表面層を少なくとも有することが好ましく、さらにその中間層を有することも好ましい。中間層は錫含有メッキ層を下地層に直接設けると「はんだ食われ」現象等を起こさせる場合に設けられ、下地層は無電解メッキ膜そのものでも良いが、導電体粉末を含有する導電ペーストの塗布膜でも良く、さらには蒸着膜、イオンプレーティング膜、スパッタリング膜その他の不良導体表面に金属層を形成できるものはいずれも使用できる。これらの膜には、 Au 、 Ag 、 Pd 、 Ag-Pd 、 Cu 、 Zn 、 Ni その他これらの合金等の金属材料を用いることができる。一般的には Ag 、 Ag-Pd 又は Pd の導電材料ペースト膜の焼付け膜からなる導電層の下地層、 Cu 又は Ni 又は Pd を主成分とするメッキ膜の中間層、さらにその上に錫含有メッキ層を有し、錫含有メッキ層が露出している構造、あるいは Cu

又はNi又はPdを主成分とする導電体を含有する導電材料ペースト膜の焼付け膜からなる下地層に錫含有メッキ層を有し、その錫含有メッキ層が露出している構造の電極が挙げられるが、これらに限らない。錫含有メッキ層とはSnのみを主成分とするメッキ層、SnとPbを主成分とし、Sn/Pb=85~98/2~15のはんだメッキ層が挙げられる。

【0012】本発明において、「複数の導電層の少なくとも1層」とは、例えば上記下地層、中間層、錫含有メッキ層の表面層を設ける場合はその少なくとも一つの層が挙げられ、したがって各単独層、任意の2つの層又は全部の層の場合が挙げられる。その少なくとも1層が本発明に係わる無電解メッキ膜であれば良く、他の層は上*



そのためメッキ膜の析出の際にCu₂Oが共析し、その微量のCu₂Oがその膜中の結晶粒界に存在することになり、これが②~④式の水素(H₂)により還元されてCuとなる際に結晶粒界に亀裂を生じさせ、延性を低下させると考えられる。ここでメッキ液中の酸素量を増や*



また、熱処理によりメッキ膜の延性が向上するのは、メッキ膜中に吸蔵された水素が加熱されることにより放出、拡散されることによりメッキ膜中の水素の吸蔵量の低下によるCu₂Oの還元能力が低下し、その還元によるCuの量が少なくなるため結晶粒界に亀裂を生じさせることが少なくなると考えられる。

【0014】

【実施例】次に本発明の実施例を説明する。

実施例1

(a) 図1に示すように、内部電極1とセラミック誘★

CuSO₄・5H₂O 8.75g/l(リットル)

ロッシェル塩 37.50g/l

NaOH 11.30g/l

ホルムアルデヒド 8.5ml/l

これに上記5万個の試験片を浸漬し、空気中10rpm(回/分)の回転速度で攪拌し、これを30分継続し、上記焼付け導電膜4の上に無電解銅メッキ膜5(膜厚1~5μm)を形成した。この際無電解メッキ液中の酸素濃度(g/l)を無攪拌の場合、酸素を吹き込んだ場合とともに図2に示す。

(c) このように処理した上記5万個の試験片を取り出し、水洗した後、容量100リットルの電解バレルメッキ槽に収容し、さらに市販のニッケルメッキ浴(例えば硫酸ニッケル六水塩250g/リットル、塩化ニッケル六水塩45g/リットル、ホウ酸30g/リットルを含有するワット浴)を80リットル入れ、浴温60℃、陰極電流密度0.5A/dm²で45分間電解ニッケル

*記材料からなる厚膜導電膜、電解メッキ膜であっても良い。また、本発明において、「熱処理を行う」とは、空気等の酸化性雰囲気、中性雰囲気加熱処理を行うことであり、その加熱温度は150~250℃が好ましく、加熱時間は30~120分、特に30~60分が好ましい。加熱が不十分であると、無電解メッキ膜の延性は高くなり、硬度も低くならない。

【0013】

【作用】例えば無電解銅メッキでは、一般的にはそのメッキ液中にCu₂Oが生成するような無電解メッキ液の条件では、下記①~③、④のどちらかの反応によってメッキ液中に金属銅が析出するために無電解メッキ液は不安定となる。

※すと下記⑤式によりCu₂Oが低減し、Cu₂Oのメッキ膜中における共析が低減し、これにより水素により還元されるメッキ膜中のCu₂Oが減り、結晶粒界に亀裂を生じさせることが少なくなると考えられる。

★電体2を交互に積層したセラミック素体3の両端に、ニッケル粉末をエチルセルローズ、タービネオールと混練りしたニッケル導電ペーストをディッピング法により塗布して乾燥し、そのニッケル導電ペースト膜を800℃で焼付け、膜厚20μmの焼付け導電膜4を形成した。このようにして焼付け導電膜を形成したセラミック素体の試験片を5万個作成した。

(b) 次に、下記組成の無電解銅メッキ液を15リットル、20リットルの容器に作製した。

バレルメッキを施し、それぞれの試験片に図1中ニッケルメッキ膜6を形成した。

(d) 次いで、得られた5万個の試験片を別の100リットルのバレルメッキ槽に収容し、さらに市販のはんだメッキ浴(例えばSnを85~98%、Pbを2~15%からなるはんだを含有する浴)を80リットル入れ、浴温25℃、陰極電流密度0.5A/dm²で45分間電解はんだバレルメッキを施し、それぞれの個体に図1中はんだメッキ膜7を形成した。

【0015】このようにしてセラミック素体3の両端に焼付け導電膜4(膜厚20μm)、無電解銅メッキ膜5(膜厚1.5μm)、ニッケルメッキ膜6(膜厚2μm)及びはんだメッキ膜7(膜厚3μm)からなる外部

電極8、8を有する3.2×2.5×1.6(mm)形状のチップ状積層セラミックコンデンサを5万個作成し、その中から無作為に抜き取って測定用試験片とし、外部電極のはんだ付け時の熱応力に対する性能の評価方法の1つである半田耐熱不良率(クラック発生率)を半田耐熱試験法により測定した結果を図3に示す。また、上記無電解銅メッキ膜の延性を知るために、銅箔に無電解銅メッキ膜を形成した代用試験片について、その延性の評価方法の1つである折り曲げ試験、その延性と関係がある膜硬度を調べる膜硬度試験を行い、その結果をそれぞれ図4、5に示した。なお、各種試験法については後述する。上記において、上記(b)における無電解銅メッキ液においてロッシェル塩の代わりに例えばEDTA等の他の錯化剤を準用した場合もロッシェル塩を用いた場合に準じた結果が得られた。

【0016】実施例2

実施例1(b)において攪拌を行わなかった以外は実施例1と同様にして無電解銅メッキ膜を形成した試験片を作製し、さらに150℃、30分間空气中で加熱する熱処理を行った後、実施例1と同様に電解ニッケルメッキ、ついでのはんだメッキを行って実施例1に準じたチップ状積層セラミックコンデンサを5万個作成し、実施例1と同様に半田耐熱不良率を測定した結果を図3に示すとともに、実施例1に準じて上記と同様に熱処理した無電解銅メッキ膜を形成した代用試験片を作製し、折り曲げ試験、膜硬度試験を行った結果を図4、5に示す。

【0017】本実施例において、熱処理の条件を200℃、30分間にした以外は上記と同様にして実施例1に準じたチップ状積層セラミックコンデンサを5万個作成し、実施例1と同様に半田耐熱不良率を測定したところ、上記に準じた結果が得られた。実施例1に準じて上記と同様に熱処理した無電解銅メッキ膜を形成した代用試験片を作製し、折り曲げ試験、膜硬度試験を行った結果を図4、5に示す。さらに、熱処理の条件を表1の欄の○に該当する条件にした以外は上記と同様にして実施例1に準じたチップ状積層セラミックコンデンサを5万個作成し、実施例1と同様に半田耐熱不良率を測定したところ、上記に準じた結果が得られた。表中、○は安定した低い半田耐熱不良率(例えば10%以下)を示し、△はその効果が未処理のものに比べれば良いが不安定であることを示し、×は半田耐熱不良率が高い(例えば30%以上)ことを示す。

【0018】

【表1】

	15分	30分	60分	120分
未処理	×	×	×	×
100℃	△	△	△	△
150℃	△	○	○	○
200℃	△	○	○	○
250℃	△	○	○	△

【0019】なお、上記熱処理を空气中で行う代わりに酸素等の他の酸化性雰囲気や、中性雰囲気、例えば窒素雰囲気で行なった場合でも空气中で行なった場合に準じた結果が得られた。

【0020】実施例3

実施例1(b)と同様に無電解銅メッキ膜を形成した試験片を作製し、さらに150℃、30分間空气中で加熱する熱処理を行った後、実施例1と同様に電解ニッケルメッキ、ついでのはんだメッキを行って実施例1に準じたチップ状積層セラミックコンデンサを5万個作成し、実施例1と同様に半田耐熱不良率を測定した結果を図3に示すとともに、実施例1に準じて上記と同様に熱処理した無電解銅メッキ膜を形成した代用試験片を作製し、折り曲げ試験、膜硬度試験を行った結果を図4、5に示す。また、熱処理条件を200℃、30分にした以外は上記と同様にして得られた結果を図4、5に示す。なお、上記熱処理を空气中で行う代わりに酸素等の他の酸化性雰囲気や、中性雰囲気、例えば窒素雰囲気で行なった場合でも大気中で行なった場合に準じた結果が得られた。

【0021】比較参考例1

実施例1(b)において攪拌を行わなかった以外は実施例1と同様にしてチップ状積層セラミックコンデンサを5万個作成し、実施例1と同様に半田耐熱不良率を測定した結果を図3に示すとともに、実施例1に準じて無電解銅メッキ膜を形成した代用試験片を作製し、折り曲げ試験、膜硬度試験を行った結果を図4、5に示す。なお、攪拌を行わなかった場合の空気存在下における無電解銅メッキ液の酸素含有量は図2に示されている。

比較参考例2

熱処理の条件を表1の欄の△に該当する条件にした以外は実施例2と同様にしてチップ状積層セラミックコンデンサを5万個作成し、実施例1と同様に半田耐熱不良率を測定したところ、上記したようにその効果は不安定であった。また、熱処理の条件を表1の欄の×に該当する条件にした以外は実施例2と同様にしてチップ状積層セラミックコンデンサを5万個作成し、実施例1と同様に半田耐熱不良率を測定したところ、上記したように効果は悪かった。

【0022】実施例2、3、比較参考例1、2と同様のことを実施例1と同様に代用試験片についても行い、上記と同様にクラック発生率を測定し、その測定結果とこ

れら実施例、比較参考例で得られた折り曲げ試験結果に基づいて両者の相関関係を図6のグラフに示すとともに、同様にクラック発生率と膜硬度との相関関係を図7のグラフに示す。また、これら実施例、比較参考例から、無電解銅メッキ液中の酸素濃度と半田耐熱不良率とを求め、これらに基づいて両者の相関関係を求めた結果を図8のグラフに示す。

【0023】上記実施例、比較参考例における各試験方法は次のとおりである。

① 酸素濃度測定法

市販の測定器（東亜電波工業社製）を用いた。

② 折り曲げ試験

厚さ0.2mmの無酸素銅箔を酸洗いした後、上記各実施例、比較参考例と同様の無電解銅メッキ液に浸漬し、同様な回転速度で攪拌し、厚さ2μmの無電解銅メッキ層を形成した。このようにして得られた試験片を折り曲げた後、元に戻す動作を1回とし、無電解銅メッキ層にクラックが発生するまでの回数を折り曲げ回数とした。折り曲げた角度は当初180度にて試験したが、無電解銅メッキ層の形成過程の差が明確になり難いので90度にて行った。

③ 膜硬度試験

96%のアルミナ基板を通常の塩化パラジウム／塩化スズ溶液による活性化処理を施した後、上記各実施例、比較参考例と同様の無電解銅メッキ液に浸漬し、同様な回転速度で攪拌し、厚さ約10μmの無電解銅メッキ層を形成した。このようにして得られた試験片を微小膜硬度計を用い、荷重15gf、保持時間5秒の条件でヴィッカース硬度H_vを測定した。

④ 半田耐熱試験

上記各実施例、比較参考例のチップ状積層セラミックコンデンサの試験片を400℃の溶融はんだに5秒間浸漬した後、クラックの発生の有無を判別し、これを100個の試験片に行い、そのクラックの発生した試験片の数を調べ、その数の全体に対する割合を百分率で示し、半田耐熱不良率（クラック発生率）とした。

【0024】上記実施例、比較参考例の結果から次のことが言える。

（イ）図2から、溶存酸素濃度については、無電解銅メッキ液を攪拌すると5mg/l（ppm）となって、攪拌しない場合の1ppmに対し、5倍増加し、酸素を吹き込んだ場合（6ppm）とあまり変わらない濃度になることができる。一般的には攪拌なしの場合の溶存酸素濃度は1ppm以下であるのに対し、攪拌した場合は4～6ppmとすることができる。このように溶存酸素濃度が増加すると、上記⑤式より、無電解銅メッキ液中のCu₂Oの生成を抑制し、反応の安定化によるメッキ液の分解抑制効果が得られる。

（ロ）図3から、熱処理したものはしないものに比べ半田耐熱不良率は1/3になり、空气中攪拌した場合はし

ないものに比べ凡そ1/10になり、さらに熱処理するとそれより小さくすることがわかる。

（ハ）図4から、無電解銅メッキ液の空气中における攪拌（溶存酸素濃度増加）、熱処理により、クラックが入るまでの折り曲げ回数が増加する。つまり延性が増加した。その理由は、上記「作用」の項で説明した通りである。熱処理により効果について補足すると、無電解銅メッキ膜中には2～30nm径のボイドが $9 \times 10^{15} / \text{cm}^3$ の密度で存在することが確認されており、このボイド中の水素ガスの圧力は、 $2 \sim 4 \times 10^4$ 気圧にも達し、これがそのメッキ層を脆化させる、いわゆる水素脆化の原因の一つであるとされているが、このボイド中の水素は拡散し易いので熱処理により水素が放出され、水素吸蔵量が低下するため、無電解銅メッキ膜の延性が増加する。これはイオンマイクロアナライザーを用いて無電解銅メッキ膜中の水素を定量することにより、熱処理によって吸蔵される水素量が減少することが確かめられており、吸蔵される水素量の減少に伴って無電解銅メッキ膜の延性は向上することが明らかにされたことになる。

（ニ）図5から、無電解銅メッキ液の空气中における攪拌（溶存酸素濃度増加）、熱処理により、無電解銅メッキ膜の硬度が低下することが分かった。その理由については、上記（ロ）の延性が増加した場合と同様の理由が考えられる。無電解銅メッキ液の溶存酸素濃度とそのメッキ膜の硬度との関係については、その溶存酸素濃度が高いほどそのメッキ膜の伸び率が向上し、引っ張り強度は低下することが確かめられており、これにより塑性の変化により硬度が低下したと考えられる。従って、溶存酸素はそのメッキ膜の膜物性を左右する重要な因子であるが、この膜物性を決定する膜構造と溶存酸素の詳細な関係は未だ解明されていない。

【0025】（ホ）図6、7から、折り曲げ回数が多い、すなわち延性が高いと半田耐熱不良率が低減され、膜硬度が低いと半田耐熱不良率が低減されることが分かり、同時に延性が高くなると膜硬度が下がることが分かった。その理由は、延性が向上するということは、一般に伸び率が増加し、引っ張り強度が低下することから、無電解銅メッキ膜の伸び率の増加のため熱応力に対するそのメッキ膜の変形による膜破断までの応力吸収量が向上し、一方引っ張り強度の低下により膜の熱応力に対する変形が容易になり、これらによりそのメッキ膜の塑性変形領域を拡大して、被メッキ体による熱応力を緩和することができるためではないかと考えられる。

（ヘ）図8から、溶存酸素濃度が3g/l以上では半田耐熱不良率が5%以下と急激に少なくなり、溶存酸素濃度の半田耐熱不良率に与える影響が顕著であることがわかる。

【0026】

【発明の効果】本発明によれば、通常の酸素濃度より多い酸素を有する無電解メッキ液を用いて無電解メッキ膜

10

20

30

40

50

を形成し、あるいは通常の酸素濃度の無電解メッキ液を用いて得られた無電解メッキ膜をさらに熱処理するようにしたので、その無電解メッキ膜の延性を増加、膜硬度を低下させることができ、これによりヒートサイクル試験や熱衝撃試験における熱応力に耐えることができる無電解メッキ膜を有する、例えば外部電極を備えたチップ状電子部品を提供することができ、セラミック素体の熱履歴による外部電極のクラックや外部電極のセラミック素体からの剥離の発生を防止することができる。また、無電解メッキ膜は、塗布膜からなる厚膜の上に形成されても、電解メッキを施す場合のようにメッキ膜の膜厚がばらつくことなく、均一な膜厚が得られ、しかも積層LCチップ部品の外部電極をパレルメッキにより形成する場合のように内部の素子がインダクタであるかコンデンサであるかによりその外部電極のメッキ膜の厚さが異なるといようなこともなく、例えば無電解メッキ膜を有する外部電極を備えたチップ状電子部品をプリント基板にはんだ付けする場合にも溶融はんだの濡れを損なわないようにできる。

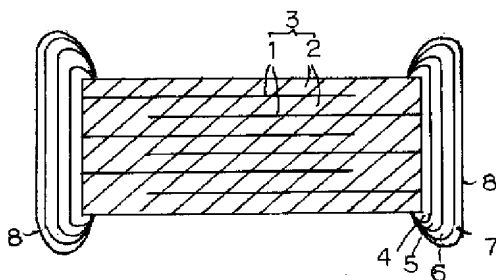
【図面の簡単な説明】

【図 1】本発明に係わる無電解メッキ膜を有する外部電極を備えたチップ状積層セラミックコンデンサの概略断面図である。

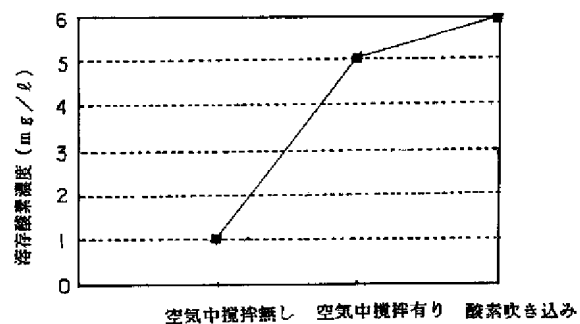
【図 2】無電解銅メッキ液中の酸素濃度を示すグラフである。

*

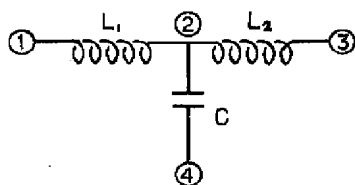
【図 1】



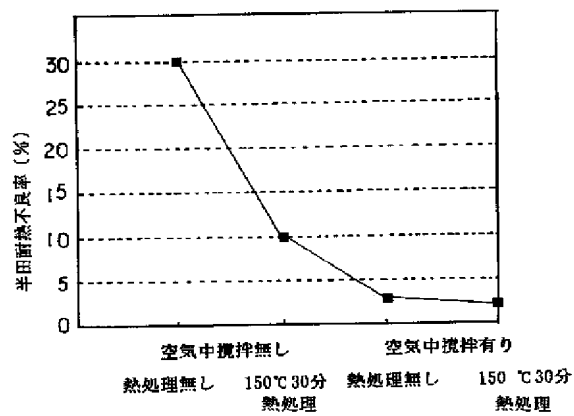
【図 2】



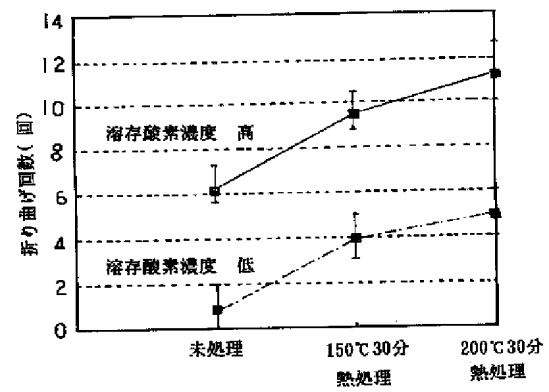
【図 9】



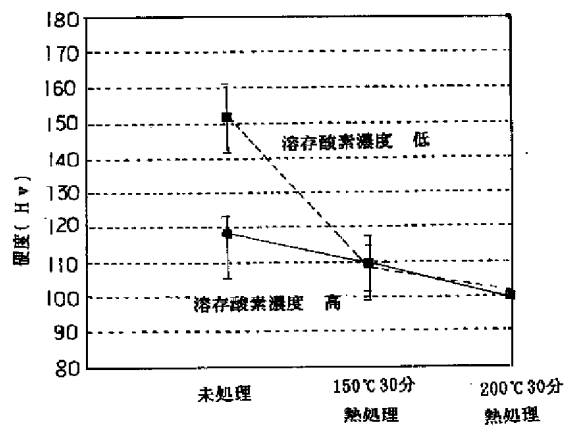
【図3】



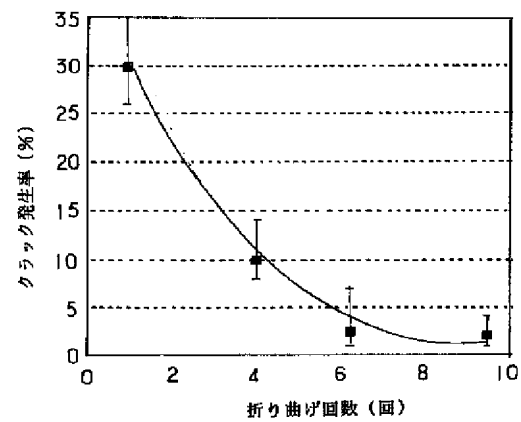
【図4】



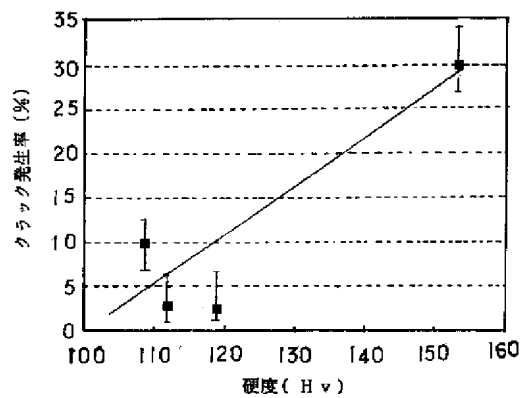
【図5】



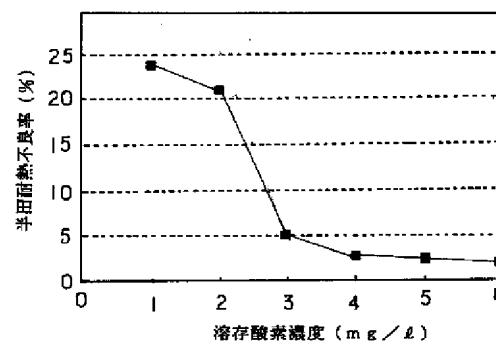
【図6】



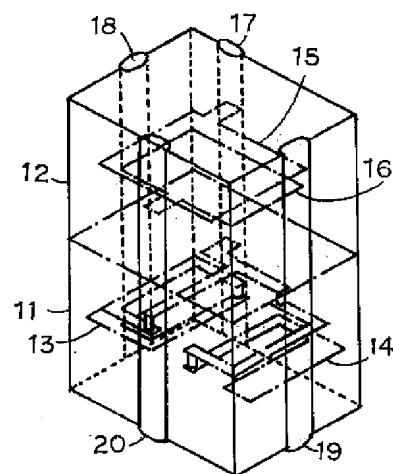
【図7】



【図8】



【図 10】



フロントページの続き

(51)Int.Cl.⁶

H 0 1 C 17/28

H 0 1 F 27/29

// H 0 1 F 41/02

識別記号

片内整理番号

F I

H 0 1 C 17/28

H 0 1 F 41/02

15/10

技術表示箇所

G

C

4230-5E

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 08-264372

(43)Date of publication of application : 11.10.1996

(51)Int.Cl.

H01G 4/12
G23C 18/16
G23C 18/52
H01C 7/02
H01C 7/04
H01C 17/28
H01F 27/29
// H01F 41/02

(21)Application number : 07-084626

(71)Applicant : TAIYO YUDEN CO LTD

(22)Date of filing : 17.03.1995

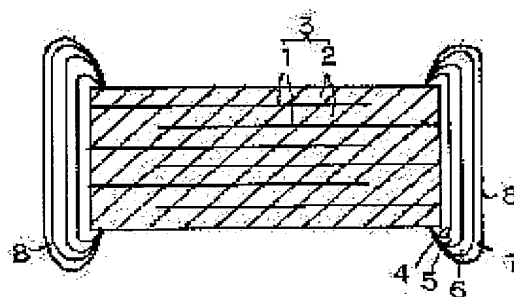
(72)Inventor : KANAI HIDEYUKI
ITO MITSUYOSHI
HONDA TOSHIMITSU

(54) MANUFACTURE OF ELECTRONIC COMPONENT WITH ELECTROLESS PLATED FILM

(57)Abstract:

PURPOSE: To reduce the variation in thickness and also lower film hardness by forming an electroless plated film using an electroless plating liquid having more oxygen than a normal oxygen concentration or having the electroless plated film obtained using an electroless plating liquid having normal oxygen concentration subjected to additional thermal treatment.

CONSTITUTION: A baked conductive film 4 is formed by applying nickel conductive paste to both ends of a ceramic material 3 comprising internal electrodes 1 and ceramic inductors 2 alternately laminated and baking them. Then the material 3 is soaked in an electroless copper plating liquid and stirred in the air to form an electroless copper plated film 5 on the conductive film 4. Then after the material is rinsed in water, electrolytic nickel barrel plating is applied in nickel plating bath to form a nickel plated film 6. This material is further subjected to electrolytic solder barrel plating in solder plating bath to form a solder plated film 7, thereby forming external electrodes 8, 8.



* NOTICES *

JP0 and INPIT are not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.**** shows the word which can not be translated.

3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1]An electroless deposition film. Oxygen below ***** dissolved oxygen usually contained in electroless plating liquid under a hyperoxia electroless deposition process formed in electroless plating liquid under air existence using electroless plating liquid which has many oxygen from quantity of usually contained ***** dissolved oxygen, and air existence. A manufacturing method of electronic parts with an electroless deposition film which have the electroless deposition film formation process of including at least one process of a heat treatment concomitant use electroless deposition process of performing stress relief heat treatment formed using electroless plating liquid to contain.

[Claim 2]A manufacturing method of electronic parts with an electroless deposition film which have an electroless deposition film formation process characterized by comprising the following.

A hyperoxia electroless deposition process formed using electroless plating liquid which has many oxygen from quantity of ***** dissolved oxygen which usually contains an electroless deposition film in electroless plating liquid under air existence.

A heat treatment process.

[Claim 3]A manufacturing method of the electronic parts with an electroless deposition film according to claim 1 or 2 whose heat treatment process is 120 minutes from 150-250 ** and 30 minutes.

[Claim 4]In a manufacturing method of electronic parts which have exterior electrodes in ceramic element assemblies at least, A manufacturing method of electronic parts with an electroless deposition film in which these exterior electrodes consist of two or more conductive layers which have a tin content metal skin in a surface layer, and at least one layer of a conductive layer of this plurality is formed of the electroless deposition film formation process according to any one of claims 1 to 3.

[Claim 5]A manufacturing method of the electronic parts with an electroless deposition film according to any one of claims 1 to 4 as for which two or more conductive layers consist of a thick film of a surface layer of a foundation layer and a tin content metal skin have two-layer at least and according [this foundation layer] to a coating film.

[Translation done.]

* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the manufacturing method of the electronic parts which have an electroless deposition film in exterior electrodes in electronic parts, such as a chip shape multilayer capacitor. [0002]

[Description of the Prior Art] Although electronic parts, such as a capacitor and an inductor, are used for many electronic equipment, The circuit component which mounted electronic parts in the printed circuit board with high density comes to be used with the miniaturization of the latest electronic equipment, Many chip like electronic components, such as a chip shape laminated ceramic capacitor, a chip shape ceramic thermo sensitive register, and a chip shape inductor, are used as electronic parts for [this] mounting with high density. These chip like electronic components form exterior electrodes in the both-ends side of ceramic element assemblies the square pillar type of each element, and pillar type, and they are used for these exterior electrodes, being soldered to the soldering land of a printed circuit board. For example, a chip shape laminated ceramic capacitor, A ceramic dielectric layer and an internal electrode are laminated by turns, and it is pulled out so that the end of the internal electrode concerned may become the both-sides end face of the ceramic element assemblies of the layered product mutually alternately in an opposite hand, The exterior electrodes linked to that end are formed in the end face concerned, and these exterior electrodes are soldered and used for the soldering land of a printed circuit board. In order to form the exterior electrodes of these chip shape laminated ceramic capacitor and other chip like electronic components, burned type conductive paste containing Ag, Ag-Pd, Cu, nickel, etc. is applied to the both-sides end face of each ceramic element assemblies, and is baked, and the foundation layer of a thick film is formed. Next, since the phenomenon of "a solder foods crack" of Ag dissolving and shifting to melting solder and slimming that baking film is produced only by this baking film when soldered to the soldering land of a printed circuit board, [what is called] Since the soldering intensity which plating metal, such as nickel and Cu, is performed on this baking film, and cannot soak melting solder in that metal skin well further, but is practical is not obtained, Plating the solder which consists of Sn for improving the wettability to melting solder on the metal skin, or Sn and Pb is generally performed.

[0003]

[Problem(s) to be Solved by the Invention] Although the metal skin of these chip like electronic components is formed of electrolytic plating, Since the metal skin is provided via a foundation layer because ceramics etc. cannot perform electrolytic plating directly nonconducting, and the foundation layer is a thick film which consists of coating films as described above, For example, in the thick film using burned type conductive paste of nickel, it is unavoidable to produce unevenness on the surface. Since the plating current density in a convex portion becomes large, a plating film will be formed thickly, the plating current density in a concave portion will become small and a plating film will be thinly formed if electrolytic plating is performed to the surface with the unevenness, What is called plating is attached, plating current density varies, the thickness of a plating film also varies according to it, a homogeneous plating film is [surroundings nature is bad,] hard to be obtained, and wettability of solder may be worsened when, soldering a chip like electronic component to a printed circuit board as a result. In the case of the T type LC circuit which connected to T type the inductor of L_1 shown

in drawing 9, and L_2 , and the capacitor of C, for example with the lamination LC chip, as shown in drawing 10, Laminate the inductor part 11 and the capacitor part 12, and connect the coils 13 and 14 of a right-and-left couple, and the former is constituted, Pinch a dielectric with the internal electrodes 15 and 16 of an up-and-down couple, and the latter is constituted, In the outer wall of the layered product at the exterior electrodes 17 corresponding to ** of LC connection section of the above-mentioned LC circuit, and the appearance L_1 , Although the thing of structure which formed the exterior electrodes 20, respectively is manufactured by each terminal of the coils 13 and 14 corresponding to terminal [of L_2] **, and ** at the terminal of the exterior electrodes 18 and 19 and the internal electrode of the capacitor similarly corresponding to terminal ** of C, Perform the exterior electrodes on a burned type conductive paste film, and what is called barrel electrolytic plating barrel electrolytic plating, A plating bath is made to intervene between the anodes which provided the negative pole into the barrel of a mesh and were provided in the exterior of a barrel corresponding to this, and the straw man of a plating object and a granular conductor is put into a barrel, and it plates, agitating these together. Therefore, if any these one flows through L_1 , terminal [of L_2] **, **, and its terminal area ** electrically with the negative pole, other terminals will flow electrically, so that it may be known also from drawing 9, but. Terminal ** of the capacitor C is electrically insulated with these, and the probability that the portion of ** will flow is set to one third in ** - **, The plating film of the exterior electrodes 20 corresponding to ** becomes thin by a plating film becoming thick, the above-mentioned exterior electrodes 17-19 corresponding to result ** - ** produce dispersion in the thickness of a plating film, and the same problem as the above is produced.

[0004]As a plating method by such an electrolytic plating method, in manufacturing a printed wired board, for example as electronic parts, Like the case where the metal layer which gives conductivity is formed in the nonconducting surfaces, such as glass, pottery, and a plastic, although the electroless plating method is used like the silver mirror reaction, Performing especially through hole plating to the hole of high integration of a semiconductor device and the byway of fine circuit formation of a printed wired board or a high aspect ratio where wiring density and the Kota stratification are called for with surface-mount-izing by non-electrolytic copper plating is performed. As a non-electrolytic copper plating film formed in a printed wired board, Temperature is performed repeatedly, or even when a temperature change is carried out rapidly, a crack goes into the plating film, or, The physical properties, i.e., the character to bear the heat stress in a heat cycle test or a spalling test, that the plating film does not exfoliate from a substrate are searched for, and it is said that it is required for ductility to be high for that purpose. However, the ductile high plating film was not obtained, but it happened that a crack arises in a plating film with the heat stress by the above-mentioned examination, or a plating film exfoliates from a substrate, and inferior goods might be made from the electroless deposition method for performing electroless deposition by the plating bath under the conventional air existence.

[0005]The 1st purpose of this invention is to provide the electronic parts with an electroless deposition film which have an electroless deposition film with little dispersion in thickness. The 2nd purpose of this invention is to provide the electronic parts with an electroless deposition film which have the electroless deposition film excellent in the wettability of solder. The 3rd purpose of this invention is to provide the electronic parts with an electroless deposition film which have an electroless deposition film with high ductility and low hardness. The 4th purpose of this invention is to provide the electronic parts with an electroless deposition film which have an electroless deposition film which can bear the heat stress in a heat cycle test or a spalling test.

[0006]

[Means for Solving the Problem]In order that this invention may solve an aforementioned problem, (1), An electroless deposition film. Oxygen below ***** dissolved oxygen usually contained in electroless plating liquid under a hyperoxia electroless deposition process formed in electroless plating liquid under air existence using electroless plating liquid which has many oxygen from quantity of usually contained ***** dissolved oxygen, and air existence. A manufacturing method of electronic parts with an electroless deposition film which have the electroless deposition film formation process of including at least one process of a heat treatment concomitant use electroless deposition process of performing stress relief heat treatment formed using electroless plating liquid

to contain is provided. A manufacturing method of electronic parts with an electroless deposition film this invention is characterized by that comprises the following. In a manufacturing method of the above (1) (3) and whose heat treatment process are 120 minutes from 150–250 °C and 30 minutes, or electronic parts with an electroless deposition film of (2), and (4) and a manufacturing method of electronic parts which have exterior electrodes in ceramic element assemblies at least, These exterior electrodes consist of two or more conductive layers which have a tin content metal skin in a surface layer, And a manufacturing method of electronic parts with an electroless deposition film in which at least one layer of a conductive layer of this plurality is formed of the above (1) thru/or one electroless deposition film formation process of (3), That for which a manufacturing method of (5), the above (1) as for which two or more conductive layers consist of a thick film of a surface layer of a foundation layer and a tin content metal skin have two-layer at least and according [this foundation layer] to a coating film, or one electronic parts with an electroless deposition film of (4) is provided.

(2), a hyperoxia electroless deposition process formed using electroless plating liquid which has many oxygen from quantity of ***** dissolved oxygen which usually contains an electroless deposition film in electroless plating liquid under air existence.

An electroless deposition film formation process of including a heat treatment process.

[0007]In this invention, although an "electroless deposition film" is a plating film obtained by plating treatment by "electroless plating liquid", the "electroless plating liquid" refers to electroless plating liquid which contains a metal ion for plating, a reducing agent, a complexing agent, and alkali chemicals at least. A metal ion for plating is ion of metal which it is going to plate to a processed material here, for example, when carrying out coppering, are a copper ion, when carrying out a nickel plate, are nickel ion, but. Electroless deposition of not only these but gold (Au), electroless deposition of platinum (Pt), Unelectrolyzed metal plating, such as silver (Ag) electroless deposition, electroless deposition of palladium, and electroless deposition of these alloy and other metal, can be performed, and metal ions, such as Au ion and Pt ion, are said in these cases. Although mineral acid ion, such as sulfate ion, nitrate ion, and a chloride ion, cyanide ion, pyrophoric acid ion, etc. are mentioned, a counter ion of these metal ions, In order to perform the supply, in the case of Cu ions, for example Copper sulfate, a cupric nitrate, a copper chloride salt, There are solutions, such as a copper cyanide and a copper pyrophosphate salt, and although especially cupric salt is preferred, other copper compounds, such as an oxide of metallic copper and copper, are dissolved in mineral acid solutions, such as sulfuric acid, and it may be made to supply, and, also in other metal ions, can carry out according to this. As concentration of a metal ion in electroless plating liquid, l. is preferred in 5g/l. – 10g /. If more than this, it will be easy to produce a metaled deposit reaction in a plating solution, and if less than this, a deposit reaction of metal of plating to a processed material will become low easily.

[0008]Although a reducing agent returns a metal ion in electroless plating liquid which it is going to plate, the metal is deposited on the processed material surface and a compound which can form a metal membrane is said, Specifically, formalin, paraformaldehyde, dimethylamine borane, hypophosphite, hydrazine, glyoxylic acid, KBH_4 , NaBH_4 , a ROSSHOERU salt, etc. are mentioned.

These can be independent or can be used together. [two or more] As concentration of a reducing agent in electroless plating liquid, l. is preferred in 0.1g/l. – 20g /. If more than this, it will be easy to produce a metaled deposit reaction in a plating solution, and if less than this, a deposit reaction of metal of plating to a processed material will become low easily. As alkali chemicals, hydroxide of alkaline metals, such as NaOH, KOH, and LiOH, is preferred, and it is preferred to add so that the pH of a plating solution may be set to 11.0–13.0. Although a complexing agent says a substance which can form a complex, Specifically, for example A tartrate, EDTA (ethylenediaminetetraacetic acid), NTA (nitriloic acid acetic acid), HEDTA(oxyethylethylenediamine triacetic acid) DHEDDA (dihydroxyethyl ethylenediamine diacetate), 1,3PDTA (1,3-propenediamine tetraacetic acid), DTPA (diethylenetriamine pentaacetic acid), It is compounds, such as TTHA (triethylenetetramine 6 acetic acid), HIMDA (hydroxy ethylimino 2 acetic acid), and ammonia, and a compound which can form a transition metal and complexes, such as metal, especially Cu, is mentioned. It is also preferred to use stabilizer for electroless plating liquid, and as this stabilizer, DDCN (sodium diethyldithiocarbamate), KSCN (thiocyanogen-ized potassium), A 2,2'-bipyridyl, 2,2'-JIPRIJIN, nicotinic acid, thiourea, Tetra methylthio urea, cupron, a cupferron, a thiazole, 2-mercaptobenzothiazole, Potassium ferrocyanide,

potassium ferricyanide, a sodium cyanide, Pyrrole, a pyrazole, imidazole, 1,2,4-triazole, 1,2,4-benzotriazol, a thiophene, a CHIOME lid, rhodanine, Rubeanic acid, pyridine, triazine, a Methyl Orange, benzoquinoline, It is preferred to add cyanide compounds, such as 2,2'-biquinoline, a dithizone, diphenylcarbazide, NEROKU pro yne, 2 (2-pyridyl) imidazoline, 1, and 10-phenanthroline, a nitrogen system organic compound, sulfur compounds, etc., and these are independent, or more than one are used together. As concentration of a stabilizing agent in electroless plating liquid, 0.01-100 ppm is preferred. If more than this, it will be easy to suspend a plating reaction to a processed material, and if less than this, the plating reaction will become difficult to occur.

[0009]In this invention, "quantity of ***** dissolved oxygen usually contained in electroless plating liquid under air existence" is the quantity of oxygen contained in the plating solution, when performing plating treatment using electroless plating liquid, and as for the concentration, 1 ppm or less are mentioned. With quantity "electroless plating liquid which has more oxygen" of the dissolved oxygen. Although it says changing the oxygen into more states than 1 ppm by specifically carrying out bubbling of air or the oxygen into electroless plating liquid, blowing ozone, or making hydrogen peroxide contain etc., for example, 4-6 ppm is mentioned, What can exist not only when it is dissolved oxygen, but in the electroless plating liquid may be used, and it pressurizes in that case and may be made to raise a dissolved amount. If there is too little quantity of this oxygen, the ductility of an electroless deposition film will not become high, and since hardness will oxidize in the plating film itself if it does not become low but there is, it is not preferred. [too much]

[0010]Although wiring boards, such as a printed-circuit board which has wiring density and an electroless deposition film for through holes of a hole of a byway of fine circuit formation for the Kota stratification or a high aspect ratio as electronic parts, and electronic parts which have exterior electrodes at least are mentioned to ceramic element assemblies in this invention, It is mentioned by chip shape ceramic electronic component especially as the latter, and to these. A chip shape cylindrical capacitor, a chip shape resistor, a chip shape ferrite bead inductor, They are mentioned by NTC or a PTC type chip shape thermo sensitive register, a chip shape varistor, chip shape laminated electronic part, etc., and as a chip shape laminated electronic part, A chip shape laminated ceramic capacitor, a chip shape lamination ceramic inductor, a chip shape lamination ceramic transformer, chip shape lamination ceramic LC parts, etc. are mentioned. "Electronic parts" can also be used as "electronic parts which has a circuit which builds in a capacitor and an inductor, and through which between each exterior electrodes flows electrically, and a circuit electrically intercepted in a direct current." Although the ceramic element assemblies refer to what made a subject a baking body of a charge of a ceramic material in this invention, A resistor, a cover body according [a case of a ferrite bead] to a magnetic body of a conductor when electronic parts using this are thermo sensitive registers, In the case of a layered product, a lamination ceramic inductor, and a lamination ceramic transformer with which a ceramic layer was laminated on both sides of an internal electrode in the case of a laminated ceramic capacitor, a layered product which laminated a ceramic layer on both sides of an inner conductor is said, and ceramic element assemblies of other electronic parts also apply to these.

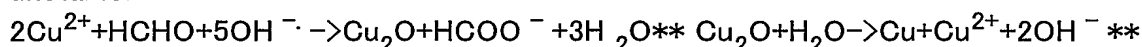
[0011]In this invention, not only when it has exterior electrodes, for example to both ends of the above-mentioned ceramic element assemblies, but when it has an insulator layer in ceramic element assemblies between exterior electrodes, it says, "It has exterior electrodes in ceramic element assemblies at least." As for exterior electrodes, it is preferred to have at least a foundation layer of a conductive layer formed in ceramic element assemblies and a surface layer of a tin content metal skin, and it is also preferred to have the interlayer further. It is provided, when an interlayer provides a tin content metal skin in a foundation layer directly and it makes a "solder foods crack" phenomenon etc. cause, Although the electroless deposition film itself may be sufficient as a foundation layer, each thing which a coating film of conductive paste containing conductor powder may be sufficient as, and can form a metal layer in the other vacuum evaporation film, ion plating film, sputtering film, and bad-conductors surface further can be used. these films -- Au, Ag, Pd, Ag-Pd, Cu, Zn, and nickel and others -- metallic materials, such as an alloy of these, can be used. A foundation layer of a conductive layer which generally consists of a baking film of an electrical conducting material paste film of Ag, Ag-Pd, or Pd, It has a tin content metal skin an interlayer of a plating film which uses Cu, nickel, or Pd as the main ingredients, and also on it, Although it has a tin content metal skin in a foundation layer which consists of a baking film of an electrical conducting

material paste film containing a conductor which uses as the main ingredients structure which a tin content metal skin has exposed, Cu, nickel, or Pd and an electrode of structure which the tin content metal skin has exposed is mentioned, it does not restrict to these. With a tin content metal skin, a metal skin, and Sn and Pb which use only Sn as the main ingredients are used as the main ingredients, and a solder metal skin of Sn/Pb=85-98/2 - 15 is mentioned.

[0012]In this invention, with "at least one layer of two or more conductive layers", when providing a surface layer of the above-mentioned foundation layer, an interlayer, and a tin content metal skin, for example, the at least one layer is mentioned, therefore a case of each single layer, two arbitrary layers, or all layers is mentioned. At least one of them is just an electroless deposition film concerning this invention, and other layers may be thick film conducting films and electrolytic plating films which consist of the above-mentioned material. In this invention, "it heat-treats" is heat-treating by oxidizing atmospheres, such as air, and neutral atmosphere, as for the cooking temperature, 150-250 °C is preferred, and, as for especially cooking time, 30 to 60 minutes is preferred for 30 to 120 minutes. The ductility of an electroless deposition film does not become it high that heating is insufficient, and hardness does not become low, either.

[0013]

[Function]For example, in non-electrolytic copper plating, on condition of electroless plating liquid which Cu_2O generally generates in the plating solution, since metallic copper deposits in a plating solution by one of the reactions of following ** and **, electroless plating liquid becomes unstable.



$\text{Cu}_2\text{O} + 2\text{HCHO} + 2\text{OH}^- \rightarrow 2\text{Cu} + \text{H}_2 + 2\text{HCOO}^-$ - Cu_2O carries out an eutectoid in the case of a deposit of H_2 **

$\text{Cu}^{2+} + 2\text{HCHO} + 4\text{OH}^- \rightarrow \text{Cu} + \text{H}_2 + 2\text{HCOO}^- + 2\text{H}_2\text{O}$ **, therefore a plating film, It is thought that a little the Cu_2O will exist in the grain boundary in the film, the grain boundary is made to produce a crack when it is returned by hydrogen (H_2) of ** - ** type and this serves as Cu, and ductility is reduced. If the amount of oxygen in a plating solution is increased here, Cu_2O will decrease by following ** type, the eutectoid in the plating film of Cu_2O decreases, it decreases in Cu_2O in the plating film returned by hydrogen by this, and it is thought that making the grain boundary produce a crack decreases.

That the ductility of a plating film improves by $\text{Cu}_2\text{O} + 2\text{H}_2\text{O} + 1/2\text{O}_2 \rightarrow 2\text{Cu}^{2+} + 4\text{OH}^-$ ** and heat treatment, The reduction ability of Cu_2O due to the fall of the occlusion amount of hydrogen in a plating film declines by being emitted and spread by heating the hydrogen by which occlusion was carried out into the plating film, and since the quantity of Cu by the reduction decreases, it is thought that making the grain boundary produce a crack decreases.

[0014]

[Example]Next, the example of this invention is described.

As shown in Example 1 (a) drawing 1, the internal electrode 1 and the ceramic dielectric 2 to the both ends of the ceramic element assemblies 3 laminated by turns. The nickel conductive paste which kneaded nickel powder with ethyl cellulose and terpineol was applied by the dipping method, it dried, the nickel conductive paste film was baked at 800 °C, and the baking conducting film 4 of 20 micrometers of thickness was formed. Thus, 50,000 specimens of the ceramic element assemblies which baked and formed the conducting film were created.

(b) Next, the non-electrolytic copper plating solution of the following presentation was produced in the container (15 l. and 20 l.).

CuSO_4 and $5\text{H}_2\text{O}$ 8.75 g/l (liter)

Rochell salt 37.50 g/l NaOH 11.30 g/l Formaldehyde 8.5ml/l. of the 50,000 above-mentioned specimens are immersed in this, It agitated with the revolving speed of 10 rpm (a part for time/) among the air, this was continued for 30 minutes, and the non-electrolytic copper plating film 5 (1-5 micrometers of thickness) was formed on the above-mentioned baking conducting film 4. In the oxygen density (g/l) in the electroless plating liquid in this case not being agitated, it is shown in drawing 2 with the case where oxygen is blown.

(c) After taking out and rinsing the 50,000 above-mentioned specimens processed in this way, It accommodates in an electrolysis barrel plating tub with a capacity of 100 l., and is a nickel plate bath (for example, nickel sulfate 6 250g/l. monohydrate) of further marketing. 80 l. of Watts baths containing nickel chloride 6 45g/l. monohydrate and 30g/l. of boric acid were put in, electrolysis nickel barrel plating was given for 45 minutes by 60 ** of bath temperature, and cathode-current-density 0.5 A/dm^2 , and the nickel plating film 6 in drawing 1 was formed in each specimen.

(d) 50,000 specimens produced by ranking second are accommodated in 100-l. another barrel plating tub, Furthermore, 80 l. of commercial solder plating baths (for example, bath containing the solder which consists Pb of 2 to 15% 85 to 98% in Sn) are put in, Electrolysis solder barrel plating was given for 45 minutes by 25 ** of bath temperature, and cathode-current-density 0.5 A/dm^2 , and the solder plating film 7 in drawing 1 was formed in each individual.

[0015] Bake on the both ends of the ceramic element assemblies 3, and Thus, the conducting film 4 (20 micrometers of thickness), 50,000 chip shape laminated ceramic capacitors of the 3.2x2.5x1.6 (mm) shape which has the exterior electrodes 8 and 8 which consist of the non-electrolytic copper plating film 5 (1.5 micrometers of thickness), the nickel plating film 6 (2 micrometers of thickness), and the solder plating film 7 (3 micrometers of thickness) are created, It samples at random out of it, and is considered as the specimen for measurement, and the result of having measured the solder heat-resistant defective fraction (rate of a crack generation) which is one of the valuation methods of performance to the heat stress at the time of soldering of exterior electrodes by the solder heat test method is shown in drawing 3. In order to know the ductility of the above-mentioned radio solution coppering film, about the substitution specimen which formed the non-electrolytic copper plating film in copper foil, the bending test which is one of ductile valuation methods, and the film hardness examination which investigates film hardness with the ductility and relation were done, and the result was shown in drawing 4 and 5, respectively. The various examining methods are mentioned later. In the above, the result of having applied correspondingly when other complexing agents, such as EDTA, were applied correspondingly instead of a Rochell salt in the non-electrolytic copper plating solution in the above (b) and a Rochell salt was used was obtained.

[0016] The specimen which formed the non-electrolytic copper plating film like Example 1 is produced except not having agitated in example 2 Example 1 (b), After performing heat treatment heated in 150 more ** and 30-minute interspace mind, like Example 1 An electrolysis nickel plate, Subsequently, while the result of having created 50,000 chip shape laminated ceramic capacitors which performed solder plating and applied to Example 1 correspondingly, and having measured the solder heat-resistant defective fraction like Example 1 is shown in drawing 3, The substitution specimen in which the non-electrolytic copper plating film heat-treated like the above according to Example 1 was formed is produced, and the result of having done the bending test and the film hardness examination is shown in drawing 4 and 5.

[0017] In this example, except having carried out the conditions of heat treatment in 200 ** and 30 minutes, when 50,000 chip shape laminated ceramic capacitors which applied to Example 1 correspondingly like the above were created and the solder heat-resistant defective fraction was measured like Example 1, the result of having applied correspondingly above was obtained. The substitution specimen in which the non-electrolytic copper plating film heat-treated like the above according to Example 1 was formed is produced, and the result of having done the bending test and the film hardness examination is shown in drawing 4 and 5. Except having made the conditions of heat treatment into the conditions applicable to O of the column of Table 1, when 50,000 chip shape laminated ceramic capacitors which applied to Example 1 correspondingly like the above were created and the solder heat-resistant defective fraction was measured like Example 1, the result of having applied correspondingly above was obtained. O shows the stable low solder heat-resistant defective fraction (for example, 10% or less) among front, although what is necessary is just to compare ** with a thing with the unsettled effect, an unstable thing is shown, and as for x, a thing with a high (for example, not less than 30%) solder heat-resistant defective fraction is shown.

[0018]

[Table 1]

	1 5 分	3 0 分	6 0 分	1 2 0 分
未処理	×	×	×	×
1 0 0 ℃	△	△	△	△
1 5 0 ℃	△	○	○	○
2 0 0 ℃	△	○	○	○
2 5 0 ℃	△	○	○	△

[0019]The result of having applied correspondingly when it carried out in other oxidizing atmospheres, such as oxygen, and neutral atmosphere, for example, a nitrogen atmosphere, instead of performing the above-mentioned heat treatment in the air and carried out in the air was obtained.

[0020]The specimen which formed the non-electrolytic copper plating film like 1 (b) of example 3 example is produced, After performing heat treatment heated in 150 more ** and 30-minute interspace mind, like Example 1 An electrolysis nickel plate, Subsequently, while the result of having created 50,000 chip shape laminated ceramic capacitors which performed solder plating and applied to Example 1 correspondingly, and having measured the solder heat-resistant defective fraction like Example 1 is shown in drawing 3, The substitution specimen in which the non-electrolytic copper plating film heat-treated like the above according to Example 1 was formed is produced, and the result of having done the bending test and the film hardness examination is shown in drawing 4 and 5. The result obtained by making it be the same as that of the above is shown in drawing 4 and 5 except having carried out the heat treatment condition in 200 ** and 30 minutes. The result of having applied correspondingly when it carried out in other oxidizing atmospheres, such as oxygen, and neutral atmosphere, for example, a nitrogen atmosphere, instead of performing the above-mentioned heat treatment in the air and carried out in the atmosphere was obtained.

[0021]While the result of having created 50,000 chip shape laminated ceramic capacitors like Example 1 except not having agitated in comparison reference example 1 Example 1 (b), and having measured the solder heat-resistant defective fraction like Example 1 is shown in drawing 3, The substitution specimen which formed the non-electrolytic copper plating film according to Example 1 is produced, and the result of having done the bending test and the film hardness examination is shown in drawing 4 and 5. The oxygen content of the non-electrolytic copper plating solution under the air existence at the time of not agitating is shown in drawing 2.

When 50,000 chip shape laminated ceramic capacitors were created like Example 2 except having made the conditions of comparison reference example 2 heat treatment into the conditions applicable to ** of the column of Table 1 and the solder heat-resistant defective fraction was measured like Example 1, the effect was unstable as described above. When 50,000 chip shape laminated ceramic capacitors were created like Example 2 except having made the conditions of heat treatment into the conditions applicable to x of the column of Table 1 and the solder heat-resistant defective fraction was measured like Example 1, the effect was bad as described above.

[0022]It performs that it is the same as that of Examples 2 and 3 and the comparison reference examples 1 and 2 about a substitution specimen as well as Example 1, The rate of a crack generation is measured like the above, and while both correlation is shown in the graph of drawing 6 based on the measurement result and the bending-test result obtained by these examples and a comparison reference example, the correlation of the rate of a crack generation and film hardness is similarly shown in the graph of drawing 7. The result of having asked for the oxygen density and solder heat-resistant defective fraction in a non-electrolytic copper plating solution, and having searched for both correlation from these examples and a comparison reference example based on these is shown in the graph of drawing 8.

[0023]Each test method in the above-mentioned example and a comparison reference example is as follows.

** The measuring instrument (made by Toa Electronics, Ltd.) of oxygen density measuring method marketing was used.

** After pickling oxygen-free-copper foil with a bending-test thickness of 0.2 mm, it was immersed in the same non-electrolytic copper plating solution as each above-mentioned example and a comparison reference example, and agitated

with the same revolving speed, and the 2-micrometer-thick non-electrolytic copper metal skin was formed. Thus, after bending the obtained specimen, operation to return was made into 1 time, the number of times until a crack occurs in a non-electrolytic copper metal skin was bent, and it was considered as the number of times. Although the bent angle was examined at 180 degrees at the beginning, since the difference of the morphosis of a non-electrolytic copper metal skin could not become clear easily, it carried out at 90 degrees.

** After performing activation according the alumina substrate of 96% of a film hardness examination to the usual palladium chloride / tin chloride solution, it was immersed in the same non-electrolytic copper plating solution as each above-mentioned example and a comparison reference example, and agitated with the same revolving speed, and the non-electrolytic copper metal skin about 10 micrometers thick was formed. Thus, Vickers hardness H_V was measured for the obtained specimen using the minute film hardness meter on load 15gf and the conditions for retention time 5 seconds.

** After the specimen of the chip shape laminated ceramic capacitor of solder heat test above-mentioned each example and a comparison reference example is immersed in 400 ** melting solder for 5 seconds, The existence of generating of a crack was distinguished, this was performed to 100 specimens, the number of the specimens which the crack generated was counted, percentage showed the whole number rate of, and it was considered as the solder heat-resistant defective fraction (rate of a crack generation).

[0024]The following thing can be said from the result of the above-mentioned example and a comparison reference example.

(**) It increases 5 times from drawing 2 to 1 ppm when becoming 5 mg/l (ppm) and not agitating about dissolved oxygen concentration, if a non-electrolytic copper plating solution is agitated, and can be made the concentration which is seldom different from the case (6 ppm) where oxygen is blown. Generally, to being 1 ppm or less, the dissolved oxygen concentration in the case of having no churning can be 4-6 ppm, when it agitates. Thus, if dissolved oxygen concentration increases, from the above-mentioned ** type, generation of Cu_2O in a non-electrolytic copper plating solution will be controlled, and the decomposition depressor effect of the plating solution by stabilization of a reaction will be acquired.

(**) When a solder heat-resistant defective fraction is set to one third from drawing 3 compared with what what was heat-treated does not carry out, and it agitates among the air, and about 1/10 is set to 10 compared with what is not carried out and it heat-treats further, it turns out that it is made smaller than it.

(**) The number of times of bending until a crack enters increases from drawing 4 by churning (dissolved oxygen concentration increase) in the air of a non-electrolytic copper plating solution, and heat treatment. That is, ductility increased. The reason is as the paragraph of the above "OPERATION" having explained. If supplemented about an effect by heat treatment, it will be checked that the void of the diameter of 2-30 nm exists by the density of $9 \times 10^{15}/cm^3$ in a non-electrolytic copper plating film, Although it is one of the causes of what is called hydrogen embrittlement by which the pressure of hydrogen gas in this void also reaches $2 - 4 \times 10^4$ atmospheric pressure, and this embrittles that metal skin, Since it is easy to be spread, and hydrogen is emitted by heat treatment and a hydrogen storage capacity falls, the ductility of an electroless deposition film increases hydrogen in this void. It means that it is confirmed by heat treatment that the hydrogen quantity by which occlusion is carried out decreases, and it was shown clearly that the ductility of a non-electrolytic copper plating film improved with reduction of hydrogen quantity by which occlusion is carried out when this quantified hydrogen in a non-electrolytic copper plating film using an ion microanalyzer.

(**) From drawing 5, churning (dissolved oxygen concentration increase) in the air of a non-electrolytic copper plating solution and heat treatment showed that the hardness of a non-electrolytic copper plating film fell. About the reason, the same reason as the case where the ductility of the above-mentioned (**) increases can be considered. About the relation of the dissolved oxygen concentration and the hardness of a plating film of a non-electrolytic copper plating solution, the pace of expansion of the plating film improves, so that the dissolved oxygen concentration is high, falling is confirmed and tensile strength is considered that hardness fell by plastic change by this. Therefore, although dissolved oxygen is an important factor which influences the film property of that plating film, the detailed relation between the membrane

structure which determines this film property, and dissolved oxygen is not yet solved.

[0025](**) There was much number of times of bending, namely, from drawing 6 and 7, when ductility was high, the solder heat-resistant defective fraction was reduced, when film hardness was low, it turned out that a solder heat-resistant defective fraction is reduced, and when ductility became high simultaneously, it turned out that film hardness falls. Generally a pace of expansion increases that ductility of the reason improves, Since tensile strength falls, the stress absorbed amount to the film fracture by modification of the plating film to heat stress improves for the increase in the pace of expansion of a non-electrolytic copper plating film, On the other hand, the modification over membranous heat stress becomes easy due to the fall of tensile strength, the plastic deformation area of the plating film is expanded by these, and it is thought that it is because heat stress with the body to be plated can be eased.

(**) It turns out that the influence which dissolved oxygen concentration decreases at not less than 3 g/l as rapidly [a solder heat-resistant defective fraction] as 5% or less, and has on the solder heat-resistant defective fraction of dissolved oxygen concentration from drawing 8 is remarkable.

[0026]

[Effect of the Invention]In this invention, the electroless deposition film which formed the electroless deposition film using the electroless plating liquid which has more oxygen than the usual oxygen density, or was obtained using the electroless plating liquid of the usual oxygen density was heat-treated further.

Therefore, the ductility of the electroless deposition film can be increased and film hardness can be reduced, . Have an electroless deposition film which can bear the heat stress in a heat cycle test or a spalling test by this. For example, the chip like electronic component provided with exterior electrodes can be provided, and ** which prevents generating of the exfoliation from the crack of the exterior electrodes by the heat history of ceramic element assemblies or the ceramic element assemblies of exterior electrodes is made.

Even if an electroless deposition film is formed on the thick film which consists of coating films, The thickness of a plating film does not vary like [in the case of performing electrolytic plating], uniform thickness being obtained, and, without it seeming that it will obtain and say if the thickness of the plating film of the exterior electrodes differs by whether an internal element is an inductor like [in the case of moreover forming the exterior electrodes of a lamination LC chip by barrel plating], or it is a capacitor, For example, also when soldering the chip like electronic component provided with the exterior electrodes which have an electroless deposition film to a printed circuit board, it can avoid spoiling **** of melting solder.

[Translation done.]

* NOTICES *

JP0 and INPIT are not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.**** shows the word which can not be translated.

3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1]It is an outline sectional view of the chip shape laminated ceramic capacitor provided with the exterior electrodes which have an electroless deposition film concerning this invention.

[Drawing 2]It is a graph which shows the oxygen density in a non-electrolytic copper plating solution.

[Drawing 3]It is a graph which shows the result of having measured the solder heat-resistant defective fraction of the specimen which has a non-electrolytic copper plating film.

[Drawing 4]It is a graph which shows the bending-test result of the specimen which has a non-electrolytic copper plating film.

[Drawing 5]It is a graph which shows the measurement result of the film hardness of the specimen which has a non-electrolytic copper plating film.

[Drawing 6]It is a graph which shows the relation of the bending-test result of a specimen and solder heat-resistant defective fraction which have a non-electrolytic copper plating film.

[Drawing 7]It is a graph which shows the relation of the measurement result of the film hardness of a specimen and solder heat-resistant defective fraction which have a non-electrolytic copper plating film.

[Drawing 8]It is a graph which shows the relation between the oxygen density in a non-electrolytic copper plating solution, and the solder heat-resistant defective fraction of the specimen which has the non-electrolytic copper plating film.

[Drawing 9]It is a T type LC circuit diagram.

[Drawing 10]It is a lamination LC chip incorporating the circuit.

[Description of Notations]

1 Ceramic dielectric layer

2 Internal electrode

3 Ceramic element assemblies

4 Printing conducting film

5 Non-electrolytic copper plating film

6 Nickel plating film

7 Solder plating film

8 Exterior electrodes

[Translation done.]